350. *The Spectrum, Fluorescence, and Photochemical Decomposition of Acraldehyde.*

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THE correlation of photochemical measurements with observations on fluorescence and absorption spectra has rapidly advanced in recent years, but the mechanism of the photochemical decomposition of aldehydes and ketones is still uncertain. The earlier work of Henri and his collaborators on the absorption spectra of aldehydes (*Compt. rend.*, various papers; *Leipziger Vorträge*, 1931, **131**; Henri and Schou, *Z. Physik*, 1928, **49**, 774; de Hemptinne, *J. Phys. Radium*, 1928, **9**, 357) has been supplemented by measurements on fluorescence (Leighton and Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165; 1933, **55**, 1766; Herzberg and Franz, *Z. Physik*, 1932, **76**, 720; Noyes, *J. Chem. Physics*, 1934, **2**, 654, 717; Norrish *et al.*, J., 1934, 1456). Photochemical measurements have been made by Bowen and Watts (J., 1926, 1607), Norrish (J., 1932, 1518; 1933, 119, 1533; 1934, 874, 1456), Damon and Daniels (*J. Amer. Chem. Soc.*, 1933, **55**, 2363), Leermakers (*ibid.*, 1934, **56**, 1537), Smith (*Carnegie Inst. Rep.*, 1928, **27**, 178), Leighton and Blacet (*loc. cit.*), and Bowen (J., 1934, 1503, 1505).

Hypotheses regarding the mechanism of the photochemical decomposition and polymerisation of these compounds have been discussed, *e.g.*, by Norrish (*Trans. Faraday Soc.*, 1931, **27**, 391, 404; 1934, **30**, 103), Mecke (*ibid.*, 1931, **27**, 359; 1934, **30**, 200), and Noyes (*Rev. Mod. Phys.*, 1933, **5**, 280). There seems to be no doubt that decomposition occurs *via* a process of "predissociation." Although many investigations favour the idea that free radicals are produced in the primary act of dissociation, this must still be accepted with reserve. Perhaps the most striking feature of the reactions is their very low quantum efficiency. In order to account for this, it has been suggested (*Proc. Roy. Soc.*, 1934, **146**, *A*, 260) that a process of "delayed" dissociation may be involved, allowing the possibility of deactivation or polymerisation before decomposition. An alternative, though not very different, view (Bowen, *loc. cit.*) is that the excited state A attained after the absorption of light is inactive, and it is necessary that the molecule shall pass into a second state B before becoming unstable. The long life of the unreactive state A will give rise to fluorescence, and will facilitate deactivation by collision or polymerisation.

It is clear that further work with other aldehydes and ketones is desirable. The present paper deals with the photolysis of acraldehyde vapour. Its absorption spectrum has been examined by Lüthy (*Z. physikal. Chem.*, 1923, **107**, 285), and the products obtained on illumination with ultra-violet light by Berthelot and Gaudechon (*Compt. rend.*, 1910, **151**, 1351). Otherwise no relevant data are on record.

EXPERIMENTAL.

The acraldehyde was purified as described in the preceding paper.

The spectrographs used for measurements of the absorption spectrum were a Hilger E315 instrument and, for greater dispersion, EI. The acraldehyde vapour was contained in a cylindrical glass tube of variable length, with plane polished quartz ends cemented on. The continuous source was a hydrogen discharge tube.

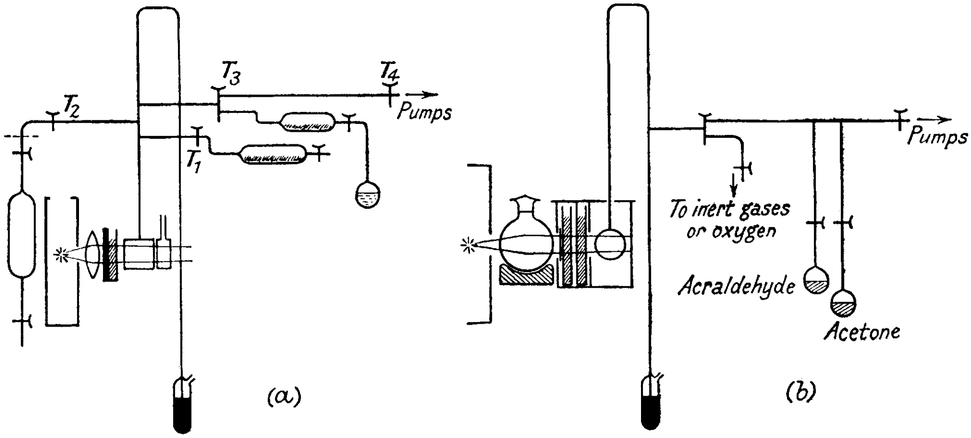
In the fluorescence measurements, light of the desired frequency was allowed to impinge perpendicularly upon the side of a cylindrical quartz vessel 4 cm. in diameter and 5 cm. long. The vessel was viewed along its axis through the plane polished ends. The cell was enclosed in one compartment of a blackened box constructed in the manner shown (Fig. 1*b*) and the incident light could be filtered by interposing solutions held in cells in the other compartment. The pressure of the vapour was measured on a mercury manometer. The source of light was either a mercury-vapour lamp or a carbon arc. With the former, the filters used were as described by Bowen (J., 1932, 2236; 1934, 76). Cuprammonium sulphate and Chance's black glass transmitted light of wave-length 3665 Å., and a solution of cobalt and nickel sulphates wave-lengths shorter than 3340 Å. For wave-lengths *ca.* 3800 Å., the carbon arc was used in conjunction with 2 cm. of *N*/100-potassium permanganate, and Chance's black glass. This combination of filters transmits the intense cyanogen band at 3883 Å. For the fluorescence measurements the acraldehyde was repeatedly fractionated in a vacuum.

The apparatus used for the photochemical work is shown in Fig. 1*a*. The quartz reaction cell was a cylinder 5 cm. in length, having plane polished ends 4 cm. in diameter. It was connected *via* capillary tubing and a ground joint (sealed with wax) to a mercury manometer, and to the remainder of the apparatus. A tube containing phosphoric oxide was attached to the reaction vessel and could be disconnected at T_1. In entering the cell the acraldehyde vapour passed over phosphoric oxide. The apparatus was evacuated by a mercury diffusion pump backed by an oil pump. The quantum efficiency was determined by employing a solution of oxalic acid as actinometer, Leighton and Forbes's values for the quantum efficiency of the sensitised decomposition of the acid (*J. Amer. Chem. Soc.*, 1930, **52**, 3139) being used. Wave-lengths 3665 and 3135 Å. were obtained by filtering the light of a mercury lamp, on the one hand, through cuprammonium sulphate and Chance's black glass, and, on the other, through a solution of nickel chloride and one of potassium hydrogen phthalate as described by Bowen.

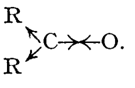
The extent to which the change of pressure recorded on the manometer is a measure of the disappearance of acraldehyde was investigated by a method closely similar to that described in the preceding paper.

The Spectrum.—The absorption spectrum was measured, pressures of 1—150 mm. being used in columns up to 1 m. in length. It has an extremely complicated structure, and only those features of the analysis which are relevant to the present investigation will be given here.

FIG. 1.



The first region of absorption extends from *ca.* 3800 to *ca.* 2900 Å., and is characteristic of carbonyl compounds; it was studied by Lüthy, with whose measurements ours are in agreement. A second and much stronger region of absorption begins at *ca.* 2330 Å. and extends to shorter wave-lengths. This far ultra-violet region at first appeared continuous, but by using longer columns and lower pressures a few narrow diffuse bands can be seen at the long wave-length end of the continuum at intervals of *ca.* 300 cm.$^{-1}$. Scheibe, Povenz, and Linström (*Z. physikal. Chem.*, 1933, *B*, **20**, 283) have referred to a region of discrete banded absorption by ketones in the region of 2000 Å. This may apply here, the system of conjugated double bonds causing a minor displacement towards the red, as occurs in the case of the longer-wave region. On the other hand, the far ultra-violet absorption may involve electronic excitation of the C=C link.

The maximum absorption in the region 3800—2900 Å. occurs at *ca.* 3450 Å. At higher pressures, the middle of the region develops into one of continuous absorption, but this is probably caused by an overlapping of bands. At lower pressures, bands can be observed over the entire range. If a continuous background such as is suggested for other aldehydes and ketones is superposed, it must be a very feeble one. The most striking feature of the band system is the occurrence of strong pairs with relatively weaker pairs interposed between them. The wave-number intervals indicate the excitation of a vibration frequency *ca.* 1260 cm.$^{-1}$. This has been found in other aldehydes and ketones, and attributed to a normal vibration of the form  ${R \atop R}\!\!>\!C\!\rightarrow\!\leftarrow\!O$. At wave-lengths longer than the first intense pair (3687, 3683 Å.), there are many sharp narrow bands which appear to degrade to the red and to have fine structure. At 3794 and 3866 Å. are very intense bands.

The most important matter from a photochemical aspect is to know whether predissociation of the molecule occurs. It is definite that at any given absorbing pressure the bands at the longer-wave end are sharper than those towards shorter wave-lengths. The point at which the diffuseness is first noticed is, however, not well defined, and appears to vary over the range 3520—3600 Å. in passing from lower to higher pressures. The significance of this, taken in conjunction with the fluorescence measurements, is discussed below.

Fluorescence Measurements.—The fluorescence of formaldehyde, acetone, acetaldehyde, and propaldehyde has already been referred to, and it seemed *a priori* probable that similar relationships would be found with acraldehyde. The nature of the spectrum described above might also suggest a region of fine-structured absorption and the possibility of discrete re-emission. Preliminary measurements in which acraldehyde vapour was irradiated with light of wave-length 3800—3000 Å. failed to excite fluorescence. With incident light of 3800—3700 Å., this result was rather surprising. In order to dispose of the possibility that the acraldehyde contained small traces of some impurity peculiarly efficient in quenching the fluorescence, the substance was repurified as already described; the results were unchanged.

In order to test the efficiency of the experimental method, acetone vapour was introduced into the cell. Irradiation with light of wave-length 3000—3100 Å. at once indicated the emission of the brilliant green glow reported by Norrish, by Damon and Daniels, and by Noyes. This appeared to establish the absence of fluorescence with acraldehyde, a result further substantiated as follows.

The addition of small traces of oxygen instantaneously converted the green glow of acetone into a faintly blue one, as reported by the above workers. The addition of acraldehyde to fluorescing acetone vapour also quenched the green fluorescence, leaving the blue glow. With oxygen, the green glow reappeared after an interval of some minutes, depending upon the amount of oxygen added. The attainment of the maximum intensity of the glow was, however, rapid after the first signs of it had reappeared. With acraldehyde as added substance, the glow again reappeared after an appropriate interval, but the attainment of the maximum intensity after the first signs of the green colour had appeared was very slow. This difference removes the possible, though unlikely, chance of small traces of oxygen being introduced simultaneously with the acraldehyde vapour. The latter is much less efficient than oxygen in quenching the fluorescence.

A detailed examination of the quenching of the fluorescence of aldehydes and ketones is in progress, but two matters relevant to the above should be mentioned. First, for equal pressures of oxygen or acraldehyde added to the same initial pressure of acetone, the time required for complete recovery of the green fluorescence is much greater for the latter than for the former. Secondly, during the quenching of the acetone fluorescence by oxygen or by acraldehyde, a decrease in pressure occurs. It appears that in the latter case acraldehyde is being photolysed, and when it has been completely removed the glow reappears.

In order to discover whether the quenching action of acraldehyde is due to the presence in it of the double-bond system, similar measurements were made with ethylene. This had no quenching effect, and hydrogen, argon, and carbon dioxide were equally ineffective.

The results show that, if visible fluorescence of acraldehyde can be detected at all, its intensity is far below that of acetone.

Photochemical Measurements.—(1) *The products of reaction.* When acraldehyde vapour is irradiated with ultra-violet light, there is a decrease in pressure and a simultaneous deposition of a brownish-white solid. A microanalysis was made of a sample of the solid obtained by using light of wave-length 3000—3200 Å. (Found: C, 56·9; H, 7·81; O, 35·29. Calc. for acraldehyde: C, 64·29; H, 7·14; O, 28·57%). Compared with acraldehyde, therefore, the solid has a deficit of carbon but excess of hydrogen and oxygen. The most satisfactory explanation, even if somewhat strange, is to suppose that the solid is a polymeride of acraldehyde containing adsorbed water, of formula $(C_2H_4CO)_2,0{\cdot}808H_2O$ (Calc.: C, 56·9; H, 7·6; O, 35·5%). If the proportion of oxygen were slightly lowered and a little ethylene included, the figures might be brought into still closer agreement. The hygroscopic nature of substances of this type is well known.

A second sample of the solid, stored in a vacuum desiccator for a week, had C, 58·94; H, 7·41; O, 33·65 [Calc. for $(C_2H_4CO)_2,0{\cdot}564H_2O$: C, 58·94; H, 7·47; O, 33·58%]. The vacuum desiccation has therefore led to the removal of much of the adsorbed water and probably of adsorbed ethylene, and it may be concluded that the solid product is a polymeride of acraldehyde, probably $(C_2H_4CO)_2$, containing a little adsorbed ethylene.

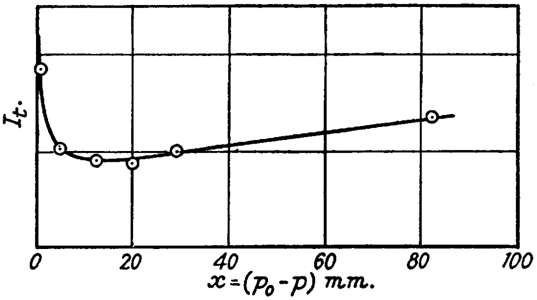
The gaseous products remaining after a prolonged illumination of acraldehyde vapour in two separate experiments were collected and analysed separately. Residual acraldehyde was first removed by washing successively with 33% caustic potash and dilute sulphuric acid, and the volume of gas remaining was measured. It was then treated with concentrated mercuric acetate solution to absorb unsaturated hydrocarbons (ethylene), and ammoniacal cuprous chloride to absorb carbon monoxide. There was a small residue. The results are as follows :

	Expt. 1.		Expt. 2.	
Total volume, c.c.	2·87	—	1·90	—
Ethylene	0·07	2·5%	0·00	0·0%
Carbon monoxide	2·7	94·0	1·85	97·0
Residue	0·1	3·5	0·05	3·0

The surprising feature of these results is the absence of ethylene or other hydrocarbons in the gaseous products in amount comparable with that of carbon monoxide. A similar conclusion was reached by Berthelot and Gaudechon. It is probable that the ethylene is adsorbed in the manner already suggested.

The residues from several analyses were mixed and examined by combustion. With the small amounts of gas obtainable, complete analysis was impossible, but the contraction of roughly 5 times the original volume, and the presence of carbon dioxide to the amount of about 3 times the original volume suggest the presence of hydrocarbons containing 2, 3, or 4 carbon atoms per molecule. The gas may be a mixture of ethane and butane.

FIG. 2.



(2) *Estimation of light absorbed.* The solid deposited during the course of the reaction forms a film on the incident face of the reaction cell. In estimating the light energy absorbed by the acraldehyde vapour it is necessary to allow for this. In an experiment with the 3665 Å. line, it was found that during the run the intensity of the light emerging from the back face of the cell at first decreased rapidly and then slowly increased. Two opposing effects are involved : on the one hand, there is an increasing thickness of the film, rapid at first but tending to a steady value, and on the other hand, acraldehyde is slowly disappearing. The amount of light energy transmitted through the cell will be proportional to $[1 - f(p_0 - p)]e^{-kp}$, where p_0 is the initial pressure of acraldehyde and p its pressure at the given instant. The expression $[1 - f(p_0 - p)]$ relates to the extinction properties of the film, and e^{-kp} is connected with extinction by the acraldehyde vapour itself. The function $f(p_0 - p)$ must be such as to increase rapidly with increasing $(p_0 - p)$ from a finite value when $(p_0 - p) = 0$, and it must approach asymptotically another finite value when $(p_0 - p)$ is large. A suitable expression for this is $\alpha(1 - e^{-\mu x})$, where $x = (p_0 - p)$. The intensity of light transmitted through the cell is then given by

$$I_t = A[1 - \alpha + \alpha e^{-\mu x}]e^{-kp},$$

which can be reduced to $$I_t = e^{-kp_0}\{a' + b'e^{-\mu x}\}e^{kx}$$

or, for a given initial pressure, $$I_t = [a + be^{-\mu x}]e^{kx}$$

The constants a, b, μ, and k can be determined empirically from the experimental data.

The light energy passing through the front face of the cell will then be given by $I = (a + be^{-\mu x})e^{kp_0}$, and that absorbed by the vapour by $I_f - I_t$.

Fig. 2 shows the plot of I_t as a function of x for a run with light of wave-length 3665 Å. The most suitable constants are found to be $a = 0·91$, $b = 0·80$, $\mu = 0·56$, and $k = 0·0037$. The following table shows the calculated and the experimental values of I_t for various values of x ; the agreement is satisfactory over the entire run.

x, mm.	0	2	4	10	20	40	60	80
I_t, obs.*	1·72	1·16	1·01	0·95	0·97	1·04	1·13	1·23
I_t, calc.	1·71	1·18	1·01	0·95	0·98	1·05	1·14	1·22

* I_t is expressed in terms of c.c. of standard oxalic acid solution decomposed in unit time.

In this way a curve may be drawn showing the relationship between $(I_f - I_t)$ and x ; this is required for the estimation of the quantum efficiencies.

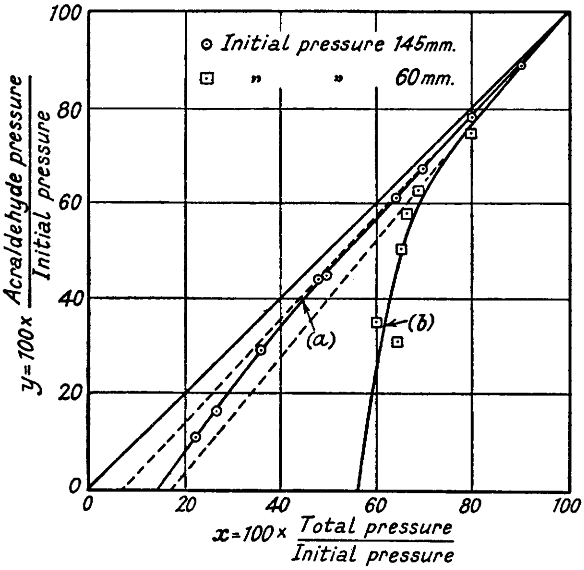
Similar expressions were found for the subsequent runs.

(3) *The relation between pressure decrease and disappearance of acraldehyde.* This was examined by the method outlined previously, in the following circumstances: (1) with initial pressures of 140—150 mm. and light of wave-length 3000—3200 Å.; (2) with initial pressures of 60 mm. and similar light; (3) with initial pressures of 140—150 mm. and light of wave-length 3665 Å. The results of Expts. (1) and (2) are summarised below:

	Initial press., p_0, mm.	Final press., mm.	Acraldehyde press., mm.	Final press., % p_0.	Acraldehyde press., % p_0.
(1)	142	130	127	91·6	89·5
	149	119	116	79·8	77·8
	152	105	103	69·0	67·7
	155	98	95	63·2	61·3
	149	70	66	47·0	44·3
	143	67	63	46·9	44·0
	143	51	43	35·7	30·1
	117	32	21	27·3	17·9
	148	33	17	22·3	11·5
(2)	61	48	46	78·6	75·5
	58	39	37	67·2	63·7
	56	36	32	64·2	57·2
	55	35·5	27	64·6	49·1
	57	34	20	59·6	35·1
	55	35	16	63·6	29·1

The figures of col. 4 are obtained by knowing the pressures of acraldehyde equivalent to 1 c.c. of iodine. If the figures of col. 5 for Expt. (1) are plotted as ordinates against those of col. 4 as abscissæ, a curve (*a*, Fig. 3) is obtained which, although at first nearly linear, cuts the abscissa axis at a noticeable distance from the origin. If only solid products were formed in the photolysis, the line would pass through the origin. The results consequently imply that gaseous products are formed, but that the polymerisation to solid products is predominant. That the curve is not linear but falls away during the later stages of the reaction, would be expected if the absorption of light energy leads to excited molecules of long life. At the higher pressures there will be more molecular collisions leading to polymerisation, and at lower pressures a greater tendency for unimolecular decomposition. This hypothesis is borne out by the results of Expt. (2).

FIG. 3.



Owing to the greater difficulties of analysis at the lower pressures used here the curve for Expt. (2) (Fig. 3, curve *b*) is less satisfactory, but it is clear that it lies below the previous one, *i.e.*, the tendency for dissociation is greater at the lower pressures.

Some results of similar measurements with light of wave-length 3665 Å. are given below:

Initial press., p_0, mm.	Final press., mm.	Acraldehyde press., mm.	Final press., % p_0.	Acraldehyde press., % p_0.
144	110	106	76·4	73·6
142	75	73	52·9	51·5
145	68	65	46·9	44·8
143	49	45	34·3	31·5
144	31	29	21·5	20·2

The curve in this case lies above that obtained above with light of higher frequency and corresponding initial pressures, which implies that the higher the frequency the greater the ratio of the amounts of dissociation and polymerisation.

(4) *Quantum efficiencies.* The quantum efficiency of the decomposition was first determined. It is necessary to obtain an expression by use of which the rate of production of carbon monoxide may be obtained from the rate of total pressure decrease. If no decomposition giving gaseous products occurred, the equation of the line of Fig 3 would be $y_2 = x$; actually it is $y_1 = mx + c$. Then $y_2 - y_1 = (1 - m)x - c$. For light 3665 Å. and initial pressure 150 mm., $(y_2 - y_1) = 0$ when $x = 100$, and $(y_2 - y_1) = 1{\cdot}5$ when $x = 50$. Then $m = 1{\cdot}03$ and $c = -3$, so that $(y_2 - y_1) = 3 - 0{\cdot}03x$. Then, if p_0 is the initial pressure, p the total pressure at the given instant, p_a the partial pressure of acraldehyde, and p_{CO} that of carbon monoxide

$$(y_2 - y_1) = 100(p - p_a)/p_0.$$

Now, the analyses given previously show that carbon monoxide formed 95% of the gaseous products. Therefore

$$105p_{\mathrm{CO}}/p_0 = 3 - 0{\cdot}03 \times 100p/p_0$$

i.e., $$p_{\mathrm{CO}} = 0{\cdot}029p_0 - 0{\cdot}029p$$

therefore $$dp_{\mathrm{CO}}/dt = -0{\cdot}029\, dp/dt.$$

A similar expression for the results at wave-length 3135 Å. involves the proportionality constant $-0{\cdot}067$.

Table I shows the course of a run at room temperatures with light of wave-length 3665 Å., t being in minutes and $-\Delta p$ in mm. The barometric pressure was measured at frequent intervals during the run and the pressures suitably corrected.

TABLE I.

Initial pressure = 131·5 mm. Temperature = 17°.

t.	$-\Delta p$.	t.	$-\Delta p$.	t.	$-\Delta p$.	t.	$-\Delta p$.	t.	$-\Delta p$.	t.	$-\Delta p$.
0	0·0	118	1·0	305	10·0	468	20·7	622	31·9	1387	82·9
17	0·0	144	1·9	332	11·5	489	22·0	640	33·3	1423	84·3
38	0·1	210	4·6	374	14·3	510	23·5	668	35·7	1470	84·9
57	0·4	230	5·6	412	16·6	539	25·7	696	38·1	1505	85·9
77	0·6	247	7·1	444	18·9	597	30·0	1355	82·0	1542	86·7
98	0·7	281	8·7								

After the vapour of acraldehyde had been introduced, it was allowed to remain for 2 hours before irradiation in order to show that the thermal polymerisation was negligibly slow. There are slight indications of autocatalysis during the early stages of a run, but we do not think that this is of significance.

The method of calculating the quantum efficiency is as follows. When the pressure has fallen 20%, *i.e.*, by 26·3 mm., the rate of pressure decrease is 4·36 mm./hr. Therefore, during the interval of 2 hrs., one hour before and one after the point of 20% pressure decrease, the fall in pressure is 8·72 mm. During this period the light absorbed was equivalent to 0·75 c.c. of N/10-permanganate. This corresponds to $0{\cdot}78 \times 10^{-4}$ g.-mol. quantum. Now a change of 8·72 mm. total pressure in 2 hours is equivalent to the production of $8{\cdot}72 \times 0{\cdot}029$, *i.e.*, 0·253 mm., of carbon monoxide in the same period. For a volume of cell 63 c.c. at 290° Abs., this is $8{\cdot}81 \times 10^{-7}$ g.-mol. The quantum efficiency is then $1{\cdot}13 \times 10^{-2}$.

Similar calculations made at other stages of the reaction gave a mean value of $1{\cdot}3 \times 10^{-2}$. A second run gave somewhat lower values :

Press. change, %	10	20	30	40	
$\gamma \times 10^2$	0·77	0·89	0·88	0·83	Mean 0·84

The difference may be due to the inaccuracies and complications introduced by the film, but there can be no doubt that the quantum efficiency of the decomposition with light of wave-length 3665 Å. is of the order 10^{-2}.

Table II summarises three runs at wave-length 3135 Å.

TABLE II.

Run 1. Initial press. 146 mm.				Run 2. Initial press. 148 mm.				Run 3. Initial press. 149 mm.			
Δt.	Δp.	Δt.	Δp.	Δt.	Δp.	Δt.	Δp.	Δt.	Δp.	Δt.	Δp
0	0	60	7·7	0	0	71	7·6	0	0	69	6·9
3	0·1	75	11·2	18	0·6	85	10·6	3	0	82	9·8
14	0·8	91	15·2	30	1·3	100	15·4	15	0·3	91	12·8
29	2·2	107	21·8	41	2·9	111	19·0	30	1·3	103	15·8
43	4·3	119	26·7	57	5·0	120	22·0	44	3·0	111	18·8
								60	4·4	120	22·3

A difficulty arises in calculating the quantum efficiency from the data at the above wave-length, since the reaction proceeds too rapidly to permit measurements on the extinction by the film as described for the longer wave-length. Accordingly, the light energy transmitted by the film after complete deposition was measured, and the quantum efficiency was determined by assuming either (*a*) that the deposition of the film was uniform with pressure decrease, or (*b*) that a complete film was present from the start. The actual state of affairs will lie between these limits. The results are given in the following table.

	Decrease of pressure, %.	(*a*).	(*b*).
Run 1	10	0·10	0·13
	18	0·21	0·23
Run 2	10	0·10	0·13
	14	0·14	0·14
Run 3	10	0·12	0·19
	15	0·20	0·20
	Mean	0·14	0·17

The mean of the two values is 0·15, and the agreement is satisfactory in view of the necessarily approximate nature of the method.

An estimate was also made of the quantum efficiency of the polymerisation. The rate of total pressure change dp/dt is composed of two parts, $-\,dp_{\text{poly.}}/dt$ and $dp_{\text{dec.}}/dt$, the rates of pressure change accompanying polymerisation and decomposition respectively. Now, 1 vol. of acraldehyde gives 1 vol. of carbon monoxide plus 0·05 vol. of other gases. Therefore

$$-\,dp_{\text{dec.}}/dt = (dp_{\text{CO}}/dt)/20$$

But, for the 3665 Å. line, $dp_{\text{CO}}/dt = -\,0{\cdot}029\,dp/dt$

therefore $dp_{\text{dec.}}/dt = 0{\cdot}0015\,dp/dt$

But $-\,dp/dt = -\,dp_{\text{poly.}}/dt + dp_{\text{dec.}}/dt$

therefore $dp_{\text{poly.}}/dt = 1{\cdot}0015\,dp/dt.$

Then for the experiment with wave-length 3665 Å., after 20% pressure change, $dp/dt = 8{\cdot}72$ mm. per 2 hrs., whence $dp_{\text{poly.}}/dt = 8{\cdot}73$ mm. per 2 hrs. Hence the number of g.-mols. which polymerise is $3{\cdot}04 \times 10^{-5}$ in 2 hrs. The light absorbed in this period is $0{\cdot}78 \times 10^{-4}$ g.-mol. quantum; the quantum yield is therefore 0·39. Values calculated for this wave-length at different stages of the reaction and in different runs were 0·31, 0·39, 0·48, 0·58, 0·53, 0·42, 0·27, 0·31, 0·32, 0·29, the mean being 0·39. The calculations for wave-length 3135 Å. are similar. A uniform deposition of film being assumed throughout, the mean value is 2·2, or if a completed film is present throughout, the value is 2·6, giving a most probable mean of 2·3.

DISCUSSION.

The results given above fall into line completely with those found for other aldehydes and ketones, with one exception. Whereas the nature of the absorption spectrum, the low quantum yield for decomposition, and its increase with increasing frequency of the incident light, and the tendency for polymerisation, are as might have been expected, yet there is apparently no fluorescence, even when the exciting frequency corresponds to the region of sharp bands. The photochemical measurements, in addition to the spectral data, suggest that absorption of light leads to an activated molecule which cannot easily decompose spontaneously. The process of dissociation appears to occur far less frequently than either deactivation by collision or, and more probably, polymerisation. In such circumstances, however, if an excited molecule of long life is formed, fluorescence should be detected. It might be possible to explain the observed result by supposing that the energy of activation becomes rapidly delocalised in the aldehyde molecule, *i.e.*, is internally degraded. The system of conjugated double bonds in the molecule might be responsible for this effect, which would also account for the quenching action of acraldehyde vapour on the acetone fluorescence. Further examples are being examined to test this hypothesis.

Several points relating to the experimental results should be mentioned. First, the values of the quantum efficiencies are admittedly approximate, but the approximations do not affect the order of magnitude. Secondly, if the polymerisation proceeds *via* the mechanism

$$C_3H_4O + h\nu \longrightarrow C_3H_4O^*$$
$$C_3H_4O^* + C_3H_4O \longrightarrow \text{polymeride}$$

the quantum efficiency measured should be rather smaller than 2. Several causes may contribute to the somewhat higher value found (*viz.*, 2·3), such as (i) adsorption of acraldehyde vapour by the solid polymeride, (ii) some formation of the triple polymeride. Again, it should be observed that there is a slight, if small, decomposition with light of wave-length corresponding to the sharp bands.

It would be interesting to determine the quantum efficiency in light of wave-lengths corresponding to the second shorter-wave region of absorption.

SUMMARY.

The absorption spectrum of acraldehyde vapour has been measured over the range 2000—7000 Å. Two regions of absorption have been detected, (*a*) from *ca.* 3800 to *ca.* 2900 Å., and (*b*) from 2320 Å. to shorter wave-lengths. Region (*a*) is attributable to electronic absorption by the carbonyl group. A preliminary analysis of the band system (*a*) has been made. An attempt to excite fluorescence of acraldehyde vapour by irradiation with ultra-violet light corresponding to the first region of absorption was unsuccessful. The photochemical decomposition and polymerisation have been studied with light of wave-length 3665 Å. and 3135 Å. The quantum efficiency of each rises in passing from longer to shorter wave-length, but that of the decomposition is surprisingly low. The facts are discussed in relation to current photochemical theory. The possibility of internal degradation or delocalisation of energy in the molecule is discussed.

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